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EDITORIAL

Interfaces of ionic liquids

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During the recent 15 years ionic liquids have experienced an unprecedented worldwide rising interest which is manifested in a still increasing number of publications every year. In 1997 there were less than 50 papers published in the field, and ionic liquids were definitely exotic at that time, but just 5 years later in 2002 already more than 500 papers were published. In 2011 more than 4000 papers dealt with this class of liquids and there is a still growing worldwide community doing experiments and theory with these liquids. It is remarkable that China has developed rapidly in this field, and in 2011 more than 1200 papers were published by Chinese groups alone.

During the recent maybe 4 years it has been found that ionic liquids show an interesting interfacial chemistry, and these in part unusual observations were the motivation for this Themed Issue. Rob Atkin from Newcastle University, Australia, was among the first who could show with Atomic Force Microscopy that ionic liquids form several remarkably strongly adhering solvation layers on solid surfaces.[1] His results were confirmed by Mezger *et al.*[2] and from then on a rising interest in the interfacial chemistry of ionic liquids could be observed. Seddon *et al.* found that ionic liquids can in principle be distilled[3] and Heintz *et al.* were the first ones who studied distilled ionic liquids by means of IR spectroscopy.[4] In parallel, Souda[5] and Steinrück *et al.*[6] showed that ultrathin layers of ionic liquids can be made by evaporation under the conditions of an ultrahigh vacuum and the Perspective from Steinrück (DOI: 10.1039/c2cp24087d) in this Themed Issue summarizes well the key results obtained by angle resolved X-ray photoelectron spectroscopy. UHV evaporation is quite a promising way to make impurity free ionic liquids and Behm *et al.* showed molecularly resolved STM images of an ionic liquid monolayer by temperature dependent UHV-STM.[7] Kornyshev *et al.*,[8] Fedorov[9] and Bazant *et al.*[10] showed in a series of theory papers that the interface between an electrode and an ionic liquid can be simulated. Instead of a simple double layer as is known for aqueous electrolytes, rather multilayers are observed and in a very fundamental experimental paper it was shown with a combination of *in situ* STM, *in situ* AFM and Electrochemical Impedance Spectroscopy that the interface of Au(111) with an ionic liquid with all impurities below 10 ppm is indeed built up of potential dependent solvation layers.[11] In a limited potential regime even the herringbone superstructure of Au(111) can be probed and there is a preferential adsorption of cations in the cathodic regime and of anions in the anodic regime. The electrochemical behavior is, nevertheless, remarkably complicated and the Discussion of Roling *et al.* in this Themed Issue (DOI: 10.1039/c2cp40288b) shows that care is needed in the interpretation of capacitance measurements. There can be more than one capacitive process, and temperature dependent measurements of the capacitance should be evaluated and interpreted with the highest care as artefacts are observed with single frequency measurements. A high purity of the liquids is a prerequisite for the interpretation of data obtained at interfaces and a recent paper from Coutinho *et al.* showed that the still popular liquids with BF_4^- and PF_6^- anions are quite problematic as they easily hydrolyze in the presence of water.[12] This hydrolysis is maybe the reason why contradictory results on the electrochemical double layer were obtained by different groups with this type of liquids. The papers published in the present Themed Issue show without doubt that the interfacial behavior of ionic liquids is complicated but also fascinating at the same time. Both experiments and theory have made remarkable progress in recent years and it can be expected that in 5 years from now it will be better understood why even slight modifications in the ion structure

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can have a considerable effect on the interfacial behavior of ionic liquids.

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